

**EUROPEAN PATENT SPECIFICATION**

- (3) Date of publication of patent specification: 20.05.87  
(2) Application number: 84300358.3  
(4) Date of filing: 20.01.84  
(5) Int. Cl.<sup>4</sup>: C 09 J 3/14, A 61 K 6/00, A 61 L 15/06, C 08 F 30/02

(6) Adhesive compositions.

(7) Priority: 21.01.83 JP 9170/83

(8) Date of publication of application: 08.08.84 Bulletin 84/32

(9) Publication of the grant of the patent: 20.05.87 Bulletin 87/21

(10) Designated Contracting States: DE FR GB IT NL

(11) References cited:  
FR-A-2 308 873  
GB-A-2 089 807

PATENTS ABSTRACTS OF JAPAN, vol. 6, no. 118(C-111)(998), 2nd July 1982

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Courier Press, Leamington Spa, England.

**EP 0 115 410 B1**

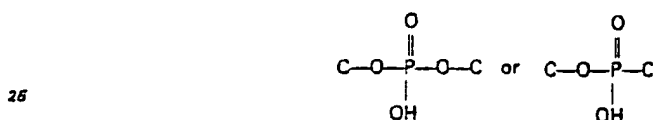
## Description

This invention relates to adhesive compositions that adhere strongly to any of the hard tissues of the living body, such as teeth and bones, metallic materials, organic polymers and ceramics, and whose adhesive strength has good water resistance. The term "adhesive compositions" as herein used not only means compositions used for bonding two or more adherends to one another, but also means compositions used for forming highly adhesive coatings on the surfaces of adherends such as metallic materials and organic polymers, and compositions used for forming highly adhesive fillings in the repair of hard tissues of the living body. In other words, the adhesive compositions to which this invention relates comprehend all compositions that exhibit adhesion to and thus are applicable to various kinds of substances, such as the hard tissues of the living body, metallic materials, organic polymers and ceramics.

Various kinds of metallic materials, organic polymers and ceramics are used for the restoration of teeth. When these restorative materials are mounted in the mouth, it is necessary to ensure the adhesion between the teeth and the metal, organic polymer or ceramic and also the adhesion of the restorative materials to each other, for example, metal to metal, ceramics or organic polymer. In particular, since dentistry involves use in the mouth, the adhesion must be satisfactory under wet conditions.

Numerous and varied attempts to use phosphate compounds in adhesive compositions have already been made in the dentistry field.

(1) U.S. Patents Nos. 4,259,075, 4,259,117 and 4,368,043 indicate that a polymerizable composition containing a vinyl compound having a group of the formula:



is effective as a dental adhesive. U.S. Patent No. 4,222,780 indicates that a polymerizable composition containing a vinyl compound having a group of the formula:



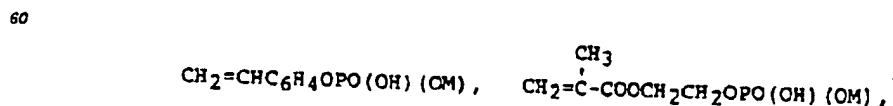
is an effective dental adhesive. Some of the compositions falling within the above patents have been widely used as primers for coating the cavity wall before a tooth cavity is filled. However, there were the problems that the cavity wall must be acid-etched beforehand in order to provide satisfactory adhesive strength to the tooth and that the adhesive strength to a Ni—Cr alloy commonly used in dentistry was not satisfactory.

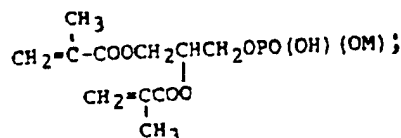
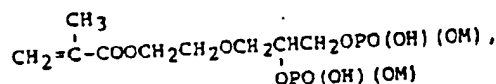
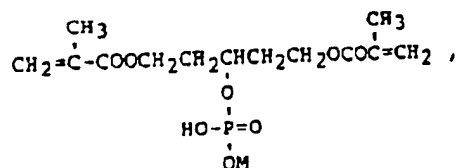
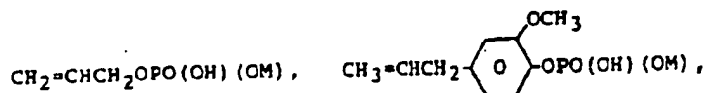
(2) Attempts to obtain adhesives having adhesion to teeth using polymerizable phosphate compounds have also been made, e.g.

- (i) U.S. Patent No. 3,882,600 describes phosphoryl monofluoride;
- (ii) Journal of Dental Research, vol. 53, p. 878-888 and vol. 56, p. 943-952, Chemical Abstract, vol. 77, p. 290 (66175 g) and Japanese Patent Application Laid-open No. 44152/1976 describe  $\text{CH}_2=\text{CH}-\text{PO}(\text{OH})_2$  and  $\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{PO}(\text{OH})_2$ ;
- (iii) Japanese Laid-open Patent Application No. 113843/1978 shows compounds obtained by neutralizing one of the two hydroxyl groups in compounds of the formula:

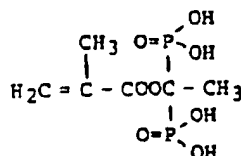


where R represents an organic residue having at least one vinyl group, specific examples of which include the following (where M represents an alkali metal):





- (iv) Japanese Patent Publication No. 49557/1982 describes methacryloyloxyethane-1,1-diphosphonic acid of the following formula:



as an adhesive component in a dental adhesive.

In the case of all the compounds described in (i) to (iv) above, high adhesive strength (especially to metals) under wet conditions cannot be obtained.

(3) Examples of other attempts to obtain adhesive compositions having adhesion to both teeth and metals include the following:

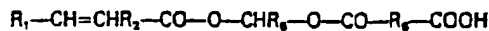
(i) U.S. Patent No. 4,148,988 shows 4-methacryloyloxyethyl trimellitate as an adhesive monomer. This monomer, however, cannot maintain a strong bond between the tooth and a metal or organic polymer material for a prolonged time in the mouth, which is under wet conditions and moreover under repeated occlusal pressure.

(ii) U.S. Patent No. 3,872,047 and Japanese Laid-open Patent Application No. 98878/1974 disclose polymers having both hydrophilic and hydrophobic groups as an adhesive component. e.g. polymers of methacryloyloxyethyl phosphate. Their adhesive strength seems adequate.

(iii) It is known that a polymer obtained by polymerizing a vinyl monomer on the tooth surface by using a ternary curing agent consisting of a peroxide, an amine and a sulphonic acid salt improves the adhesive strength to the tooth (U.S. Patent No. 4,182,035). However, no satisfactory adhesive strength can be obtained by a combination with any conventional vinyl monomer, and thus it is necessary to investigate a new adhesive vinyl monomer for this purpose.

(4) Further, attempts to use phosphate compounds in adhesive compositions have been made widely in various industries. Examples are disclosed in U.S. Patents Nos. 3,754,972, 3,884,864, 3,987,127, 4,001,150, 4,044,044, 4,223,115, Japanese Laid-open Patent Applications Nos. 20238/1974, 100596/1975, 125182/1976, 12995/1978, 11920/1981 and 44638/1982, and Japanese Patent Publication Nos. 4126/1980, 4790/1980. However, none of the phosphate compounds described in the above patent literature is free from problems associated with the retention of adhesive strength in the presence of water.

Japanese Patent Publication JP-A-5744638 discloses the production of an adhesive resin composition by forming a mixture of a polyolefin, a dibasic acid monoester of formula

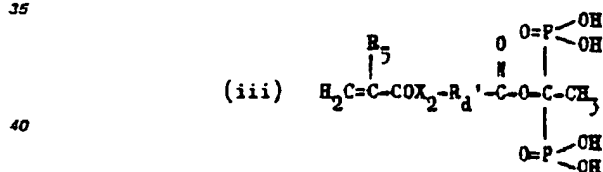
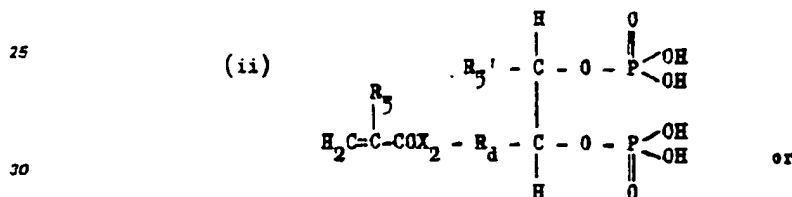
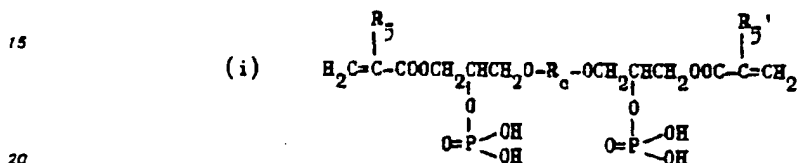


and a phosphoric ester of formula



where m is 1 or 2, n is 0 or 1, each of  $R_1$ ,  $R_2$  and  $R_3$  is hydrogen or methyl,  $R_3$  is  $-OPO(OH)_2$ ,  $R_4$  is hydrogen, chloromethyl or  $-CH_2O-CO-C(R_2)=CHR_1$ , and  $R_5$  is the residue of a dicarboxylic acid.

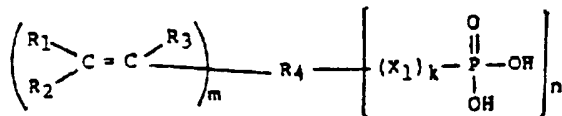
The present invention provides an adhesive composition suitable for bonding two or more adherends to one another, or for forming adhesive coatings on the surfaces of adherends, or for forming adhesive fillings in the repair of hard tissues of the living body, comprising (a) 1 part by weight of a compound of the general formula:



in which each of  $R_5$  and  $R_5'$  represents a hydrogen atom or a methyl radical,  $R_6$  represents a bivalent organic residue of 2—54 carbon atoms,  $R_d$  represents a bivalent organic residue of 4—57 carbon atoms,  $R_d'$  represents a bivalent organic residue of 3—57 carbon atoms and  $X_2$  represents O, S or  $NR_6$ , where  $R_6$  represents H or  $C_{1-4}$  alkyl, and (b) 0—199 parts by weight of a vinyl monomer copolymerizable with the aforesaid compound.

Compositions of the present invention can be used for bonding a hard tissue of the living body with another such tissue or a material for restoring the tissue (for example, a metal, an organic polymer or a ceramic material), or for filling and restoring such a hard tissue (e.g. a tooth), for coating the inside of a cavity of a tooth before filling, for bonding and fixing a tooth and a dental restorative material (e.g. inlay, onlay, abutment tooth, bridge, post, splint, orthodontic bracket or crown), for bonding dental restorative materials to each other (e.g. abutment tooth and crown), as a pit and fissure sealant for coating a tooth surface to prevent caries, for bonding metals, organic polymers and ceramics, or as adhesives in coating agents or paints to form a coating having excellent adhesion on the surface of a metal or a ceramic material.

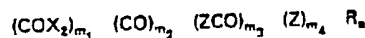
In addition, the invention provides, for use in applying to the wall of a tooth cavity before filling a dental composite resin into the tooth cavity, for use in coating the surface of a tooth for the prevention of dental caries, for use in filling a dental cavity, and for use in bonding a tooth to a dental restorative material or bonding dental restorative materials to one another, a dental adhesive composition suitable for bonding a tooth to a dental filling or for forming an adhesive coating on the surface of a tooth or for forming an adhesive filling in the repair of a tooth comprising (a) 1 part by weight of a compound of the general formula:



where each of  $R_1$  and  $R_2$ , which are the same or different, represents a hydrogen atom, a  $C_{1-6}$  hydrocarbon or halogen-substituted hydrocarbon group, a group of formula  $COOR'$  where  $R'$  represents a  $C_{1-20}$  hydrocarbon or halogen-substituted hydrocarbon group or a halogen atom;

$R_3$  represents a hydrogen or halogen atom, a  $C_{1-6}$  hydrocarbon or halogen-substituted hydrocarbon group, or a CN group, and may be the same as or different from  $R_1$  and/or  $R_2$ ;

$R_4$  represents a radical of formula:



where  $R_5$  represents a  $C_{9-50}$  organic residue having a valency of  $m + n$ , each of  $m_1$ ,  $m_2$ ,  $m_3$  and  $m_4$  represents 0, 1, 2, 3 or 4 such that  $m_1 + m_2 + m_3 + m_4 \leq m$ ,  $X_2$  represents O, S or  $NR_6$  (where  $R_6$  represents H or  $C_{1-4}$  alkyl) and Z represents O or S;

$X_1$  is as defined for  $X_2$  and may be the same as or different from  $X_2$ ;

$m$  represents 1, 2, 3 or 4;

$n$  is 2, 3, 4, 5 or 6, and

$k$  is 0 or 1;

and when  $m$  is 2 or more, each of the  $R_1$ s,  $R_2$ s and  $R_3$ s may be the same or different and when more than one  $X_1$  and/or  $X_2$  are present, each of them may be the same or different; and

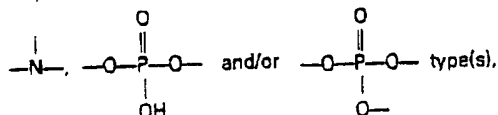
(b) 0—199 part by weight of a vinyl monomer, 0.01—20 parts by weight of a curing agent per 100 parts by weight of the polymerizable monomers [(a) + (b)], and, optionally, one or more of a redox polymerization initiator, a photosensitizer, and a volatile organic solvent having a boiling point of 150°C or below at 760 Torr (1013 Pa) in an amount not exceeding 300 times by weight that of the polymerizable monomers [(a) + (b)].

In the adhesive compositions of this invention, the above compound, which contains a (meth)acryloyl residue and two  $PO(OH)_2$  residues in the molecule, is used as an adhesive monomer imparting adhesion to hard tissues of the body, metals and ceramics. Adhesive compositions containing a compound having a (meth)acryloyl residue and a single  $PO(OH)_2$  residue in the molecule are covered by our earlier European Patent Application No. 82303942.5 (EP-A-0074708).

The term "organic residue" means:

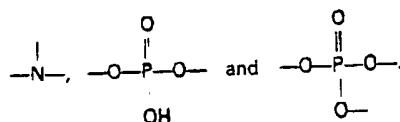
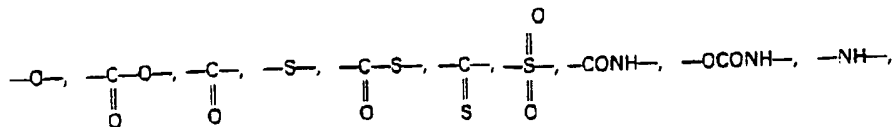
(i) a hydrocarbon group optionally containing OH, COOH,  $NH_2$  or halogen as a substituent; and

(ii) a group composed of 2 to 20 hydrocarbon groups of the type defined in (i) above connected to one another by linkages of one or more of the ether, thioether, ester, thioester, thiocarbonyl, amide, carbonyl, sulphonyl, urethane,  $-NH-$ ,

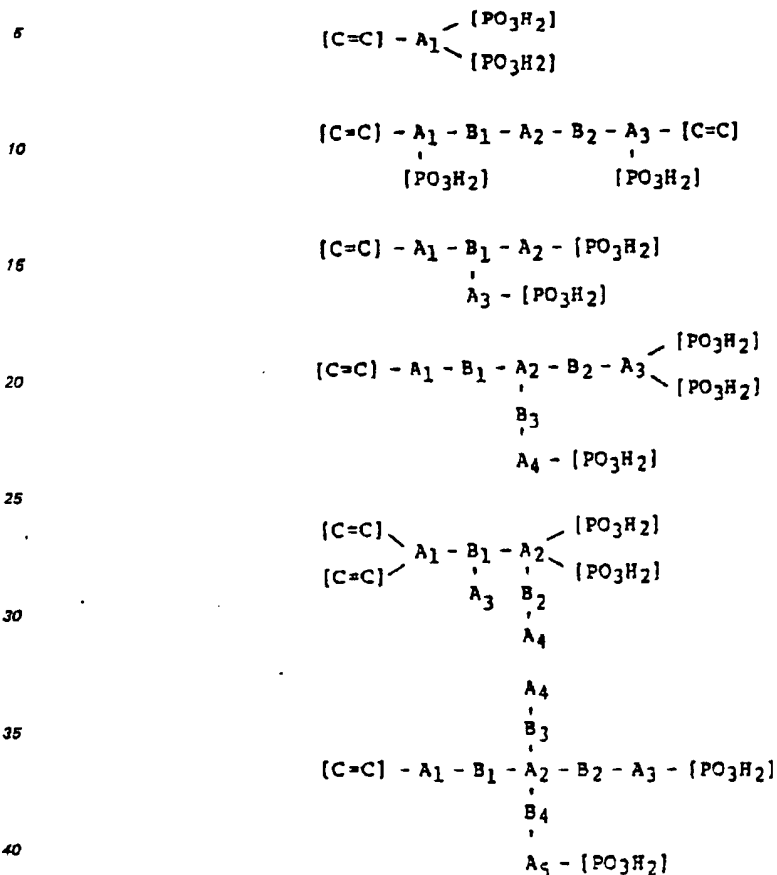


including not only those groups in which the backbone of the organic groups is composed of the hydrocarbon groups but also those in which a part of the hydrocarbon groups constitute the side-chain of the organic residue.

Applicable such organic residues are illustrated by the following formulae, in which A represents a hydrocarbon group, and B represents a linkage selected from

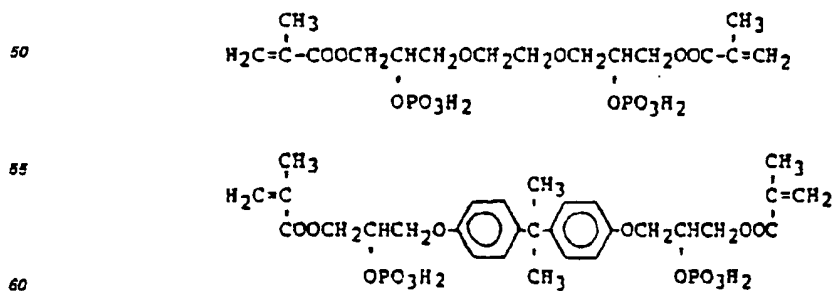


For the sake of simplicity, the double bond side is represented by [C=C], and the phosphoric or phosphonic acid side is represented by [PO<sub>3</sub>H<sub>2</sub>].

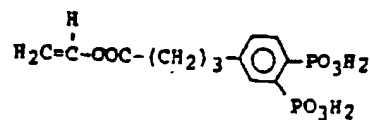
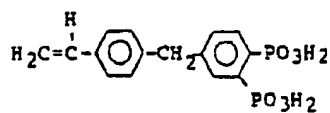
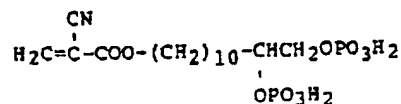
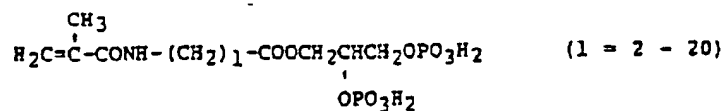
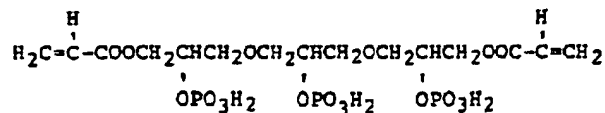
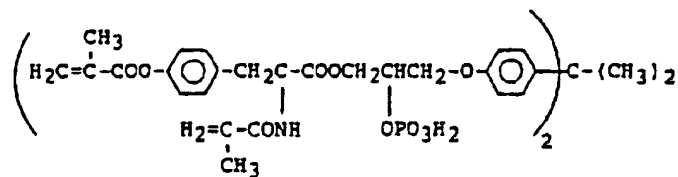
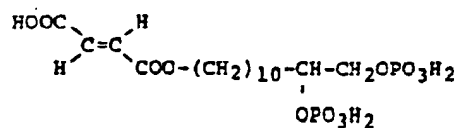
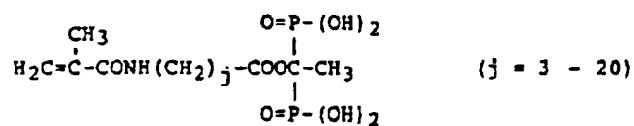
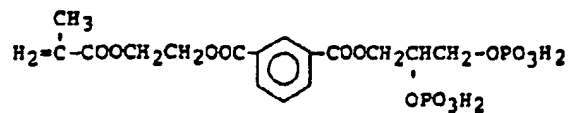
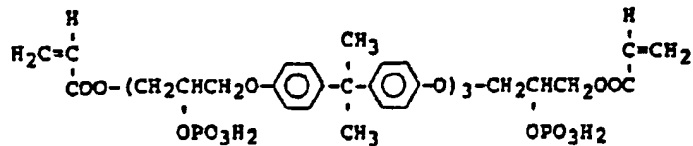


The term "hydrocarbon group" in this invention also covers a halogenated hydrocarbon group unless otherwise specified.

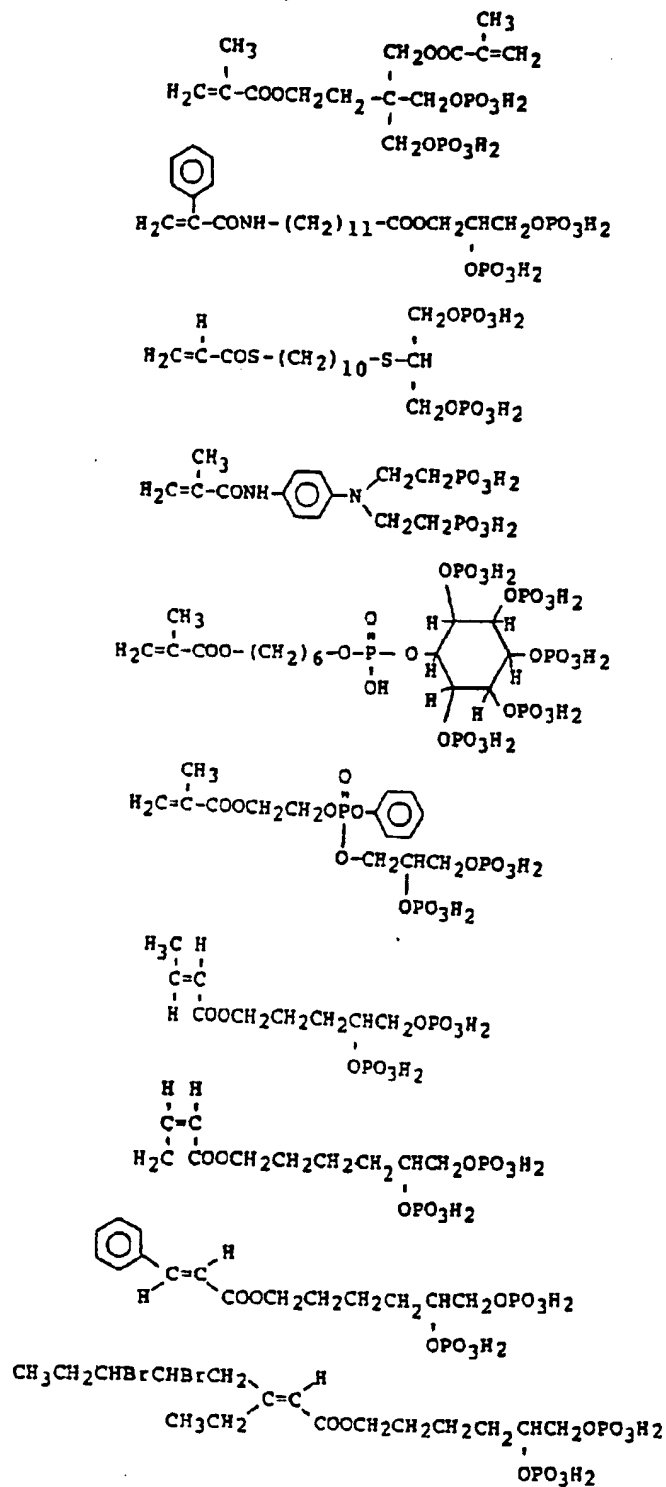
Specific examples of the adhesive monomers having two or more —PO(OH)<sub>2</sub> groups used in this invention are given below:



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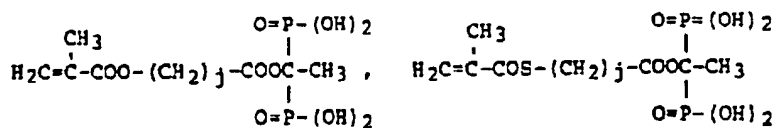
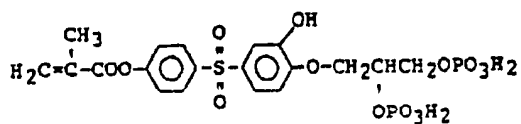
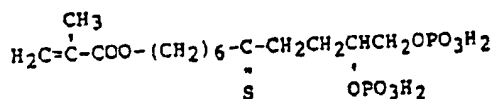
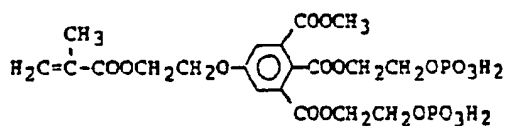
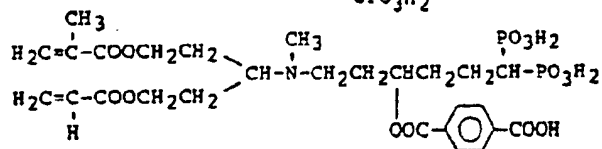
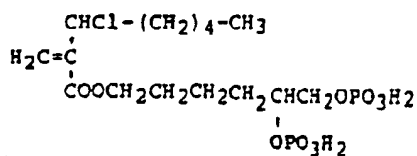
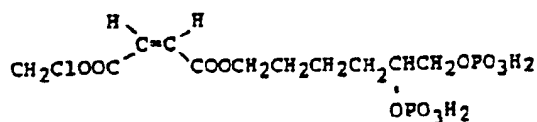
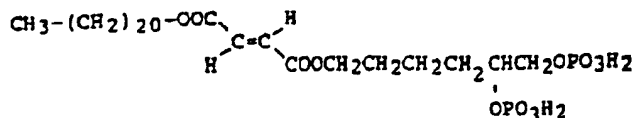


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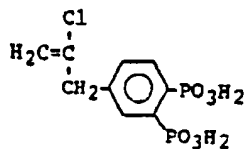
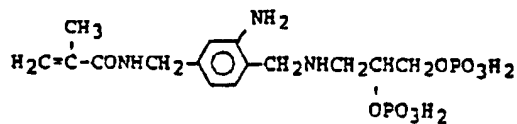


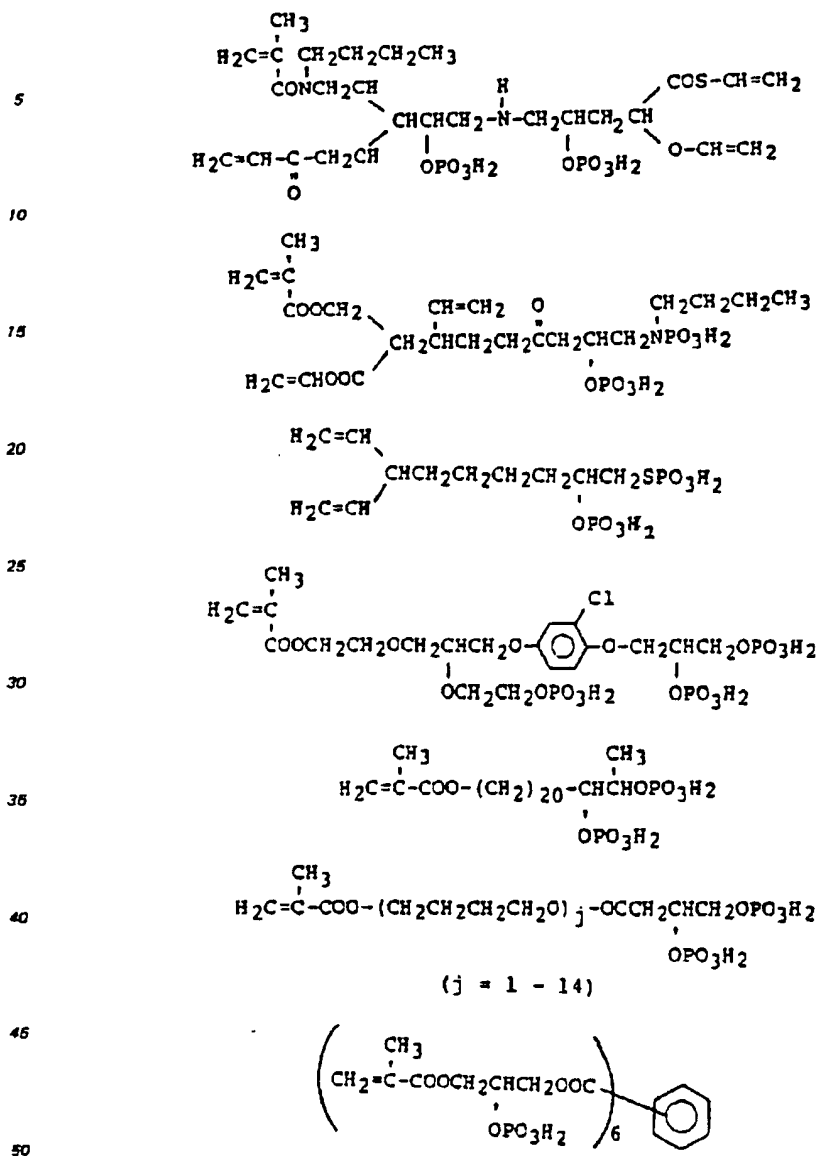


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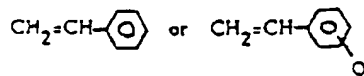




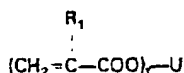
If  $R_1$  is of only one carbon atom in the compounds of the formula (i), or if  $R_1$  contains fewer than four carbon atoms in the compounds of formula (ii), or if  $R_1$  contains only one or two carbon atoms in the compounds of formula (iii), the adhesive strength to teeth and metal and like materials and its water resistance are extremely poor as compared with the compounds used in this invention. In general, there is a tendency for the adhesive strength to become higher with the increase in number of the carbon atoms in these residues. However, when the number of the carbon atoms increases and exceeds 50, the adhesive strength begins to decrease. Therefore, it is necessary that the upper limit for the carbon atoms in  $R_1$  be not greater than 54 and in  $R_2$  and  $R_3$  be not greater than 57.

In the adhesive composition of this invention (which is hereinafter sometimes referred to as the "adhesive composition"), the compound of the formula (i) is used in combination with a vinyl monomer copolymerizable with said compound. By the selection of the copolymerizable vinyl monomer, the viscosity, wettability, curability, mechanical properties etc. of the adhesive may be controlled. While the vinyl monomer is appropriately selected according to the intended purpose and use, it is general to use a (meth)acrylate type monomer, a styrene type monomer or vinyl acetate. In addition to the above,

acrylamides such as (meth)acrylamide, N-n-butoxymethyl(meth)acrylamide, N-(hydroxymethyl)-acrylamide etc., (meth)acrylic acid, isobutyl vinyl ether, diethyl fumarate, diethyl maleate, maleic anhydride, methyl vinyl ketone, allyl chloride, vinyl naphthalene, vinylpyridine etc. are also used. Examples of the above-described styrene type monomer include compounds of the formula:



wherein Q is halogen or a hydrocarbon group of 1—6 carbon atoms, e.g., divinylbenzene, p-chlorostyrene etc. As the (meth)acrylate type monomer, compounds generally often used in anaerobic adhesives, dental adhesives etc. may also be favorably used in this invention. As the (meth)acrylate type monomer, a (meth)acrylate type monomer of the formula:



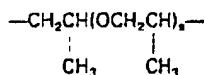
wherein R<sub>1</sub> represents H or CH<sub>3</sub>, U represents an organic group of 1—50 carbon atoms, and t represents an integer of 1—4 (for the definition of the organic group, refer to the description hereinabove) is used. Examples of such a monomer include the following:

(i) Monofunctional (meth)acrylates:

Methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, benzyl (meth)acrylate, decyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate (sometimes referred to as HEMA), 2-hydroxypropyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 3-chloro-2-hydroxypropyl methacrylate, 2,3-dibromopropyl (meth)acrylate etc.

(ii) Difunctional (meth)acrylates:

a) Those wherein U is  $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_s-$  or



wherein s is an integer of 0—15:

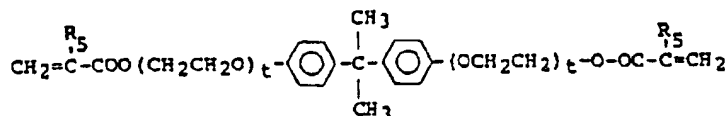
Ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate etc.

b) Those wherein U is alkylene (generally of 3—12 carbon atoms):

Propanediol di(meth)acrylate, glycerin di(meth)acrylate, 1,3-butanediol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,5-pentanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentylglycol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, 2,3-dibromoneopentyl glycol dimethacrylate etc.

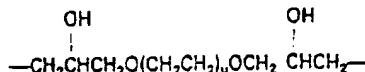
c) Those wherein U has a residue of a bisphenol A derivative:

Bisphenol A di(meth)acrylate, 2,2-bis[(meth)acryloyloxypropoxyphenyl]propane, i.e.



wherein t is an integer of 1—9, 2,2'-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane (sometimes referred to as Bis-GMA) etc. Among the above, those wherein U is of 15—30 carbon atoms are favorably employed.

d) Those wherein U is



wherein u is 1 or 2:

1,2-Bis[3-(meth)acryloyloxy-2-hydroxypropoxy]ethane, 1,4-bis[3-(meth)acryloyloxy-2-hydroxypropoxy]butane etc.

e) Urethane di(meth)acrylates wherein U is JOCONHTNHCOOJ wherein J is alkylene (generally of 2—10 carbon atoms), and T is an organic diisocyanate residue of 1—50 carbon atoms:

For example, those described in Japanese Patent Application Laid-open No. 687/1976 are employed.

(iii) Tri- and tetrafunctional methacrylates:

Trimethylolpropane tri(meth)acrylate, trimethylolthane tri(meth)acrylate, tetramethylmethane tri(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, N,N'-(2,2,4-trimethylhexamethylene) bis[2-(aminocarboxy)propane-1,3-diol] tetramethacrylate etc.

These copolymerizable monomers are used either singly or in a combination of several thereof. Of these monomers, that preferred for use in dental adhesives is a methacrylate, and it is desired that it constitutes 50% by weight or more of the copolymerizable monomer. Preferred examples of the methacrylate include methyl methacrylate, ethyl methacrylate, HEMA, n-hexyl methacrylate, benzyl methacrylate, lauryl methacrylate, Bis-GMA, bisphenol A dimethacrylate, 2,2-bis[(meth)acryloyloxypropoxyphenyl]propane, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate, 1,10-decanediol dimethacrylate, neopentyl glycol dimethacrylate, trimethylolthane trimethacrylate etc.

In the adhesive composition of this invention, it is necessary to use the compound of the formula (I) in an amount of 0.5% by weight or more, that is, to use 0—199 parts by weight of the aforesaid copolymerizable monomer per part by weight of the compound of the formula (I). With the amount of less than 0.5% by weight, the adhesive strength is inadequate. It is more preferred to use the compound of the formula (I) in an amount of 1.5% by weight or more.

The adhesive composition of this invention is applied to a surface to be bonded, and polymerized and cured either by physical means such as heating, or irradiation with X-rays or ultraviolet light or visible light, or by chemical means, e.g. using a polymerization initiator, to exhibit a bonding function. Although a certain type of the compounds (I) of this invention, that is, that wherein  $R_3$  is CN can provide a composition curable without using a curing agent, it is general to effect curing by irradiating with light in the presence of a photosensitizer or adding a polymerization initiator. In this invention, the term "curing agent" is used to include both polymerization initiator and photosensitizer. Examples of the usable curing agent are varied, for example, organic peroxides, azo compounds, organic metal compounds, redox type initiators, photosensitizers, for ultraviolet or visible light etc. Specific examples thereof include benzoyl peroxide, di-t-butyl peroxide, cumene hydroperoxide, t-butyl hydroperoxide, methyl ethyl ketone peroxide, azobisisobutyronitrile, tributylborane, organic sulfinic acids or salts thereof, hydrogen peroxide/ $Fe^{2+}$  salt systems, cumene hydroperoxide/ $Fe^{2+}$  salt systems, benzoyl peroxide/N,N-dialkylaniline derivative systems, ascorbic acid/ $Cu^{2+}$  salt systems, organic sulfinic acid (or salt thereof)/amine (or salt thereof)/peroxide systems,  $\alpha$ -diketone/allylthiourea systems (visible light type), benzoin methyl ether, benzoin ethyl ether, benzil, diacetyl, diphenyl disulfide, di- $\beta$ -naphthyl sulfide etc. Of the above, those preferred for use in dental adhesive compositions are benzoyl peroxide, azobisisobutyronitrile, tributylborane, organic sulfinic acids or salts thereof, and aromatic sulfinic acid (or salt thereof)/diacyl peroxide/aromatic secondary or tertiary amine (or salt thereof) systems. Examples of the aromatic sulfinic acids include benzenesulfinic acid, p-toluenesulfinic acid,  $\beta$ -naphthalenesulfinic acid, styrenesulfinic acid etc. The cation for forming a salt with said sulfinic acid can be, for example, an alkali metal ion, an alkaline earth metal ion, an ammonium ion etc., of which the alkali metal ion and the alkaline earth metal ion are superior in terms of storage stability and adhesive strength. Examples thereof include  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$  etc. Preferred specific examples of the aromatic amines include N,N-dimethylaniline, N,N-dimethyl-p-toluidine, N,N-diethanol-aniline, N,N-diethanol-p-toluidine, N-methylaniline, N-methyl-p-toluidine etc. These amines may also form salts with hydrochloric acid, acetic acid, phosphoric acid etc. Examples of the diacyl peroxides include benzoyl peroxide, m-toluoyl peroxide, 2,4-dichlorobenzoyl peroxide, octanoyl peroxide, lauroyl peroxide, succinic acid peroxide etc., of which benzoyl peroxide and m-toluoyl peroxide are particularly preferred. The curing agent is employed in an amount of 0.01—20 parts by weight per 100 parts by weight of the polymerizable monomer employed, especially preferably in the range of 0.1—15 parts by weight.

It is sometimes desired to add a volatile organic solvent having a boiling point of 150°C or below at 760 Torr to the adhesive composition of this invention. Such an embodiment is preferred in the case where the adhesive composition of this invention is employed as a primer used in filling a dental filling material in a tooth cavity. The volatile organic solvent thus applied is evaporated by blowing air or nitrogen, thereby a coating of the vinyl compound is formed on the adherend surface. Examples of the organic solvent suitable for such a using method include methanol, ethanol, acetone, methyl ethyl ketone, methyl acetate, ethyl acetate, dichloromethane, chloroform, diethyl ether, diisopropyl ether, toluene etc. The proportion of such a volatile solvent to the total polymerizable monomers is 300 times (by weight) or less, preferably 100 times or less. A large dilution exceeding 300 times exhibits a great reduction in the adhesive strength probably because the coating of the polymerizable monomer formed on the adherend surface is too thin.

The adhesive composition of this invention may sometimes contain a conventionally known filler of an inorganic or organic polymer or an inorganic-organic composite type. By adding the filler, the adhesive composition of this invention may be used as a dental cement for adhesion and filling, a dental composite resin and a bone cement. The amount of the filler added is up to 1000 parts by weight, preferably 20—500 parts by weight, per 100 parts by weight of the polymerizable monomer. By the addition of the filler, the rheological properties of the adhesive composition on use and the mechanical properties, adhesive strength and water resistance of the cured composition are improved. Examples of the inorganic filler used

in this invention include natural minerals such as quartz, feldstone, pottery stone, wellastonite, mica, clay, kaolinite, marble etc., ceramics such as silica, alumina, silicon nitride, boron carbide, boron nitride, glass, e.g., soda glass, barium glass, strontium glass and borosilicate glass, glass-ceramics containing lanthanum, etc., and water-insoluble salts such as barium sulfate, calcium carbonate etc. The inorganic filler is generally surface-treated with a silane coupling agent, such as  $\gamma$ -methacryloyloxypropyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltrichlorosilane, vinyltris(2-methoxyethoxy)silane, vinyltriacetoxysilane,  $\gamma$ -mercaptopropyltrimethoxysilane etc. Examples of the organic polymer filler include various polymers such as polymethyl methacrylate, polyamides, polyesters, polypeptides, polysulfones, polycarbonates, polystyrene, chloroprene rubber, nitrile rubber, styrene butadiene rubber, polyvinyl acetate etc. Examples of the inorganic-organic composite type filler include those obtained by coating the above-described silane-treated inorganic fillers with the above-described various polymers.

These fillers may be used either singly or in a combination of several thereof. The particle size of the filler is usually not greater than 100  $\mu$ m, and the shape may be either formless, spherical, lamellar or fibrous. If a polymer is used, it may also be dissolved in a polymerizable monomer or a volatile organic solvent. Where the adhesive composition of this invention is used as a dental cement or a dental composite resin, the filler is preferably an inorganic filler or an inorganic-organic composite type filler.

Further, the adhesive composition of this invention, in particular, the adhesive composition for industrial and domestic use, may be modified by dissolving an organic solvent soluble polymer such as PMMA, polystyrene, polyvinyl acetate, chloroprene rubber, butadiene rubber, nitrile rubber, chlorosulfonated polyethylene etc. in an amount of up to 200 parts by weight, preferably up to 120 parts by weight, per 100 parts by weight of the vinyl monomer composition used in this invention, to aim the thickening of said adhesive composition, the improvement of the mechanical properties of the cured composition, etc.

In addition to the above-described various components, the adhesive composition of this invention may further contain for example, a polymerization inhibitor such as hydroquinone monomethyl ether (MEHQ), an antioxidant such as 2,6-di-tert-butyl-p-cresol (BHT), an ultraviolet absorbing agent, various pigments and dyes, a phthalic acid diester, silicone oil etc., if necessary, depending on the required performance as a practical adhesive composition. These are added as small amount additives in amounts of up to 10 parts by weight, generally up to 5 parts by weight, per 100 parts by weight of the polymerizable monomers.

When the adhesive composition of this invention is used for dental, orthopedic or other medical purposes, a room temperature curing redox type initiator may often be used. In such a case, it is necessary to ensure the storage stability of the composition and hence to choose an appropriate package form which can keep the oxidant and the reducing agent apart from each other. Examples of the package form include two-part packages of (a) the vinyl compound plus the reducing agent in one and (b) the vinyl compound plus the oxidant in the other, two-part packages of (a) the vinyl compound plus the oxidant (or reducing agent) and (b) the volatile organic solvent plus the reducing agent (or oxidant), two-part packages of (a) the vinyl compound plus the oxidant (or reducing agent) and (b) the filler plus the reducing agent (or oxidant), two-part packages of (a) the vinyl compound plus the filler plus the oxidant and (b) the vinyl compound plus the filler plus the reducing agent, etc. In an organic sulfinic acid (or salt thereof)/amine (or salt thereof)/peroxide ternary system, which is particularly suitable, among the redox type polymerization initiators, for the adhesive composition of this invention, the sulfinic acid and the amine are the reducing agent and the peroxide is the oxidant. In this case, it is also possible to choose a three-part package form in which the sulfinic acid and the amine are packed separately.

Where a photosensitizer is employed as the curing agent, the vinyl compound plus the photosensitizer must be stored in a container shielded against light. Where an initiator which initiates polymerization in a short time once it is brought into contact with a vinyl compound (e.g. tributylborane etc.), it is necessary to pack the vinyl compound and the polymerization initiator separately. The thus separately packed adhesive composition is mixed together just before use.

The adhesive composition of this invention adheres excellently to any of the following materials, and maintains high adhesive strength for a long time even under wet conditions:

(1) hard tissues of the living body, such as teeth and bones;  
(2) metal materials, including not only non-precious metals such as iron, nickel, chromium, aluminum, cobalt, copper, zinc and tin, or stainless steel, brass or other alloys thereof, but also precious metal alloys containing 50—90% of gold or platinum, which have hitherto been difficult to bond with any conventional adhesive;

(3) ceramics, such as glass, porcelain, silica and alumina; and  
(4) organic polymer materials, such as polymethyl methacrylate, polyesters, polyamides, polyurethanes, polycarbonates, polysulfones, polystyrene etc.

The adhesive composition of this invention may be used in various application fields because of its excellent adhesion to various materials as described above. Preferred examples of its applications are given below:

(i) Dental applications:

An adhesive composition for coating a tooth cavity on filling and restoring said cavity with a composite

resin generally comprising a polymerizable monomer, a filler and a polymerization initiator: in general, this is supplied to dentists as a total system in which said composite resin and this adhesive composition are combined.

9 A composite resin for filling a tooth cavity: In this case, a filler is incorporated in the adhesive composition of this invention, and the obtained composition is used as a filling material and at the same time has adhesion to teeth.

An adhesive composition for bonding an inlay, onlay, crown or the like to a tooth, or maintaining a bridge, post, splint, orthodontic bracket or the like to a tooth, or bonding a crown to an abutment tooth. Pit and fissure sealant.

10 When used in the respective applications, the specific composition for the adhesive composition is chosen with reference to the description hereinabove. For example, in a case of the adhesive composition for coating a tooth cavity before filling the composite resin, it may contain 1.5—100% by weight of the aforesaid adhesive vinyl compound in the adhesive composition, diluted with another polymerizable monomer (e.g. Bis-GMA, HEMA, aliphatic dimethacrylate) or an organic solvent (e.g. ethanol) and further it  
 15 may contain room-temperature-curing agent, in accordance with the recipe shown in U.S. Patent No. 4,259,075 or 4,259,117. Where the adhesive composition is used as the composite resin, it is preferred to use that obtained by adding 1.5—50% by weight (based on the total polymerizable monomers) of the aforesaid adhesive vinyl monomer to the conventional filling material consisting of 20—40% by weight of a polymerizable monomer such as Bis-GMA etc. and 80—20% by weight of a filler. By applying the thus  
 20 obtained adhesive composition to a tooth in the conventional manner, the cured composite resin strongly adheres to the tooth, and thus the need for any mechanical retention such as an under-cut has been eliminated. [While it is desired to apply the adhesive composition of this invention after acid etching the tooth cavity surface for better adhesive strength, the adhesive composition of this invention can provide practically satisfactory adhesive strength even without such acid etching as compared with the  
 25 compositions disclosed in U.S. Patents Nos. 4,259,075 and 4,259,117, and this is advantageous since there is the risk that acid etching exerts an injurious effect on the pulp]. When an inlay, onlay, crown or the like is to be bonded to a tooth cavity or abutment tooth, it is preferred to use that having a composition of, for example, 1.5—50 parts by weight of an adhesive vinyl monomer, 98.5—50 parts by weight of a copolymerizable monomer and 50—500 parts by weight of a filler. By coating a slight excess of such an  
 30 adhesive composition on the adherend surface and bringing them into intimate contact, it is now possible to bond them to the tooth. Further, it is now possible to prevent caries by forming a film strongly adhered to the tooth surface by coating a solution containing polymerizable monomers, including an adhesive vinyl monomer, and a polymerization curing agent on the tooth surface and curing it.

### 35 (ii) Orthopedic Applications:

The adhesive composition of this invention may be employed as a bone cement for bonding and fixing a ceramic or metal artificial joint or splint to the bone. One preferred example of the composition for the adhesive composition in this case is 90—98.5 parts by weight of methyl methacrylate, 10—1.5 parts by weight of an adhesive vinyl monomer and 50—150 parts by weight of polymethyl methacrylate.

40

### (iii) General industrial and domestic applications:

Since the adhesive composition of this invention has excellent adhesion to metal materials, ceramics and organic polymer materials, it is useful as adhesives for transport machines, electric appliances, building materials, cans and ceramics, as well as for domestic use. Further, it may be used as a paint, a  
 45 primer for a paint, or a coating agent. When used in such applications, the adhesive composition of this invention has a surprising feature that it can adhere to the adherend surface even not only when it is contaminated with an oil but also with water. Moreover, the adhesive strength is markedly higher than that of any conventional polymerization curing type adhesive, such as cyanoacrylates, epoxy resins, SGA (second generation acrylic adhesives) etc.

50 Having generally described the invention, a more complete understanding can be obtained by reference to certain specific examples, which are intended for purpose of illustration only and are not intended to be limiting.

### [Examples of the Production of Adhesive Monomers Used in the Invention]

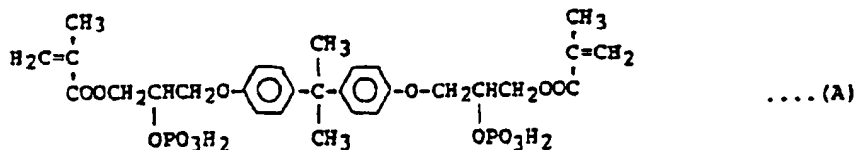
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#### Production Example 1

36 g of phosphorus oxychloride was dissolved in 100 ml of tetrahydrofuran (THF), placed in a 1-liter flask and cooled to -50°C. 50 g of Bis-GMA and 22 g of triethylamine were dissolved in THF and added dropwise thereto while maintaining the internal temperature of the flask not higher than -40°C. After the  
 60 addition, the internal temperature was allowed to rise to 0°C, 11 g of water and 49 g of triethylamine dissolved in THF were added dropwise thereto. The reaction mixture was stirred under ice-cold condition for a half day, and the separated triethylamine salt was filtered off.

A trace of MEHQ was added to the filtrate, and the solvent was evaporated under reduced pressure to obtain the following phosphate compound:

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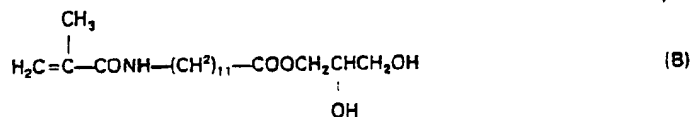
Elementary Analysis:

C = 51.3%; H = 5.1%; P = 9.0%.

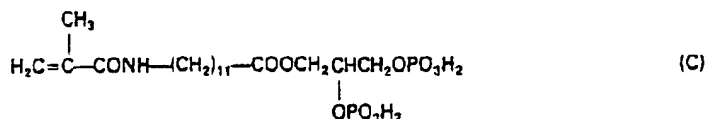
#### Production Example 2

0.3 Mole of methacrylic acid chloride and 0.3 mole of 1,2-aminododecanoic acid were reacted in a mixed solvent of dioxane and water under Schotten Baumann reaction conditions to obtain N-methacryloyl-12-aminododecanoic acid in a yield of 73%.

Then, 30 g of said compound was mixed with 30 g of glycidol and 3 g of triethylbenzylammonium chloride. The mixture was heated to 80°C to effect the reaction for 4 hours, to obtain the following compound:



The two hydroxyl groups of said compound (B) were converted to phosphate forms according to the procedures in Production Example 1 to obtain the following compound (C):



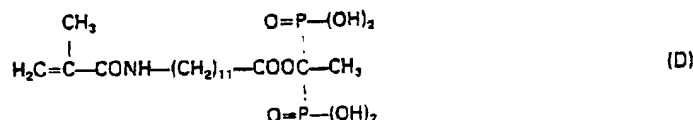
Elementary Analysis:

C = 43.6%; H = 6.9%; P = 11.9%; N = 2.1%.

#### Production Example 3

The N-methacryloyl-12-aminododecanoic acid synthesized in Production Example 2 was reacted with phosphorus pentachloride to synthesize N-methacryloyl-12-aminododecanoyl chloride.

Then, 0.1 mol said acid chloride was reacted with 0.1 mol of 1-hydroxyethane-1,1-diphosphonic acid in DMSO in the presence of 0.3 mol of triethylamine to synthesize the following compound:



Elementary Analysis:

C = 45.2%; H = 7.0%; N = 2.7%; P = 12.8%.

[Examples of the Adhesive Composition of this Invention and Use thereof]

#### Example 1

Using the compound (C) synthesized in Production Example 1, a two-pack type primer having the following composition was prepared:

##### Formulation I

Bis-GMA	50 pts. by wt.
HEMA	43
Compound (C)	7
Benzoyl peroxide	2

## Formulation II

	Ethanol	100 pts. by wt.
5	Sodium benzenesulfinate	3
	N,N-Dimethyl-p-toluidine	0.7

A human molar was imbedded in an epoxy resin in a cylindrical holder, the dental crown was cut off to expose the dentin, and this was used as a specimen for a bonding test. A stainless steel bar of 9 mm in diameter and 25 mm in length was prepared. The dentin surface and one end surface of the stainless steel bar were polished with #1000 abrasive paper, an adhesive backed tape having a hole of 5 mm in diameter was applied to the dentin surface to limit the surface area to be bonded, then equal amounts of Formulation I and Formulation II were mixed and coated thinly on both of the dentin surface and the end surface of the stainless steel bar. Immediately thereafter, air was blown onto the coated surfaces to evaporate the ethanol. A commercial dental composite resin (tradename: "Clearfil-F") was kneaded, the obtained paste was mounted on the end surface of the stainless steel stick, and this was pressed against the dentin surface to effect bonding. The specimens were immersed in water at 37°C thirty minutes after completion of the bonding operation. On the following day, measurement of tensile bond strength was made. Adhesive failure occurred at the interface between the dentin and the composite resin, and the adhesive strength was 78 kg/cm<sup>2</sup>.

## Comparative Example 1

A test on the bonding to the dentin of human teeth was conducted in the same manner as in Example 1 except that the compound (C) was replaced by a known phosphate compound, that is, 2-methacryloyloxyethyl dihydrogenphosphate to find that its adhesive strength was 13 kg/cm<sup>2</sup>.

## Example 2

As adherends, round bars (7 mm in diameter and 25 mm in length) made of iron, aluminum, copper, nickel, porcelain,  $\alpha$ -alumina, glass, polymethyl methacrylate and polycarbonate were prepared respectively. One end surface of each of these round bars was polished with #1000 abrasive paper to provide each adherend surface. A 5% ethanolic solution of the compound (D) synthesized in Production Example 3 was thinly coated on each adherend surface, and the ethanol was evaporated using an air syringe. Then, equal amounts of the following formulations for preparing a powder-liquid type adhesive composition were mixed, immediately coated on each adherend surface, and the bar of the same kind were bonded together end to end.

## Formulation III

	Methyl methacrylate	100 pts. by wt.
46	Benzoyl peroxide	1

## Formulation IV

50	Polymethyl methacrylate powder	100 pts. by wt.
	Sodium benzenesulfinate powder	3
	N,N-Diethanol-p-toluidine	1

An hour after the bonding, the bonding test specimens were dipped in water and stored at room temperature for 10 days, after which each adhesive strength under tension was measured, to obtain the following results: iron: 460 kg/cm<sup>2</sup>, aluminum: 408 kg/cm<sup>2</sup>, copper: 271 kg/cm<sup>2</sup>, nickel: 418 kg/cm<sup>2</sup>, porcelain: 225 kg/cm<sup>2</sup>,  $\alpha$ -alumina: 165 kg/cm<sup>2</sup>, glass: 108 kg/cm<sup>2</sup>, polymethyl methacrylate: 198 kg/cm<sup>2</sup>, and polycarbonate: 142 kg/cm<sup>2</sup>.

## Comparative Example 2

The bonding test same as in Example 1 was conducted except that the compound (D) was replaced by 1-methacryloyloxyethane-1,1-diphosphonic acid, to find that the adhesive strength of any of the iron, aluminum, copper, nickel, porcelain,  $\alpha$ -alumina and glass was not higher than 50 kg/cm<sup>2</sup>.



## Example 3

Using the compound (A) synthesized in Production Example 1, a powder-liquid type adhesive composition having the following composition was prepared:

## Formulation V

5	Bis-GMA	40 pts. by wt.
	2-HEMA	30
10	Neopentyl glycol dimethacrylate	20
	Compound (A)	10
	Benzoyl peroxide	2
15	MEHQ	trace

## Formulation VI

20	Silane-treated quartz powder	100 pts. by wt.
	Sodium benzenesulfinate powder	0.3
25	N,N-Diethanol-p-toluidine	0.4

The crown part of a bovine anterior tooth was imbedded in an epoxy resin in a cylindrical holder to prepare a bonding test specimen. At that time, the specimen was fixed in the holder with its labial enamel surface exposed in order to enable the bonding to said surface. The labial enamel surface was polished with #1000 abrasive paper, and then acid etched with a 40% orthophosphoric acid aqueous solution for one minute. The acid was washed away with water, and the etched tooth surface was dried by an air syringe, to prepare an adherend surface. Separately, a stainless steel round bar of 7 mm in diameter and 25 mm in length, one end surface of which had been polished with #1000 abrasive paper, was prepared. 0.1 g of Formulation V and 0.3 g of Formulation VI were mixed intimately to prepare a paste adhesive composition, this was coated on said end surface of the stainless steel round bar, and this surface was pressed against the etched tooth surface to effect bonding.

An hour after the bonding, the specimen was dipped in water at 37°C. and on the following day, the adhesive strength under tension was measured. Breakage occurred at the interface between the enamel and the adhesive composition, and the strength was 171 kg/cm<sup>2</sup>.

## Example 4

A cylindrical cavity of 4 mm in diameter and 4 mm in depth was formed on the lingual side of a human molar using a diamond bur, and the inside of the cavity was dried using an air syringe. Thereafter, an equal-amount mixed solution of Formulation I and Formulation II employed in Example 1 was coated on the entire surface of the cavity, the ethanol was evaporated by the air syringe, and a commercial dental composite resin (tradename: "Clearfil-F") was filled therein in the conventional manner. After stored in water at 37°C for a day, this tooth was dipped in dye solution baths at 4°C and 60°C, 100 times alternately, one minute in each bath, then cut using a cutter, and examined whether the dye had penetrated into the bonded interface between the tooth and the filled material. No penetration of the dye was observed.

## Example 5

A conical cavity of 6 mm in diameter and 4 mm in depth was formed on the occlusal surface of a human molar, and an inlay conforming to the size of this cavity was cast using a Type III gold alloy. Formulation V' in which the compound (A) incorporated in Formulation V in Example 3 was replaced by the compound (D) was prepared, kneaded with Formulation VI, and the obtained paste was coated on the conical surface of the inlay, which was then pressed into the cavity to effect bonding.

Ten minutes after the bonding, this was dipped in water at 37°C, and on the following day, this was subjected to a thermal cycling test comprising dipping in water baths at 4°C and 60°C alternately. The inlay still adhered strongly to the tooth even after the thermal cycling test, and when it was tried to peel off by using the edge of a knife, it was impossible.

## Example 6

A plate-formed cast of a 1 mm in thickness and fitting to the lingual surface of a human anterior tooth was prepared using a Ni—Cr alloy (Ni: 76%, Cr: 12%, Mo: 3%, others: 9%). The surface of this cast to be in contact with the tooth was sand blasted with 33  $\mu$  alumina abrasive grains. On the other hand, the lingual

surface of the human anterior tooth was etched with a 40% phosphoric acid aqueous solution for a minute.

Formulation V' in which the compound (A) incorporated in Formulation V in Example 3 was replaced by the compound (D) was prepared, kneaded with Formulation VI, then coated on the cast surface and pressed against the lingual surface of the human anterior tooth to effect bonding. Ten minutes after the bonding, the tooth was dipped in water at 37°C, and the adhesive strength under tension was measured on the following day, to obtain a value of 160 kg/cm<sup>2</sup>. The adhesive failure occurred on the human tooth side.

#### Example 7

A pit and fissure sealant having the following composition was prepared and filled into a fissure of a molar:

#### Formulation VII

15	Bis-GMA	50 pts. by wt.
	HEMA	20
	Compound (D)	20
20	Neopentyl glycol dimethacrylate	10
	Benzoyl peroxide	1.5

#### Formulation VIII

25	Bis-GMA	50 pts. by wt.
	HEMA	30
30	Neopentyl glycol dimethacrylate	20
	Sodium benzenesulfinate	2
35	N,N-Diethanol-p-toluidine	1.5

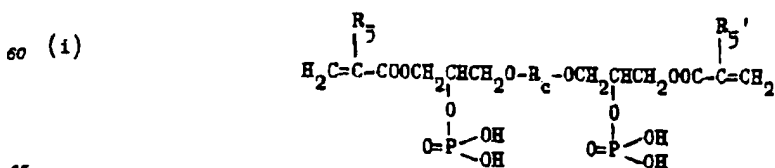
The fissure of the human molar was cleaned using an explorer, washed with water, dried, and a sealant (an equal amount mixture of Formulations VII and VIII) was filled into the fissure without etching treatment. Ten minutes after the curing, this tooth was dipped in water at 37°C. After stored under the same conditions for a day, this sample was dipped in dye solution baths at 4°C and 60°C 100 times alternately, one minute in each bath, cut using a cutter, and examined whether the dye had penetrated into the bonded interface between the tooth and the filled material. No penetration of the dye was observed.

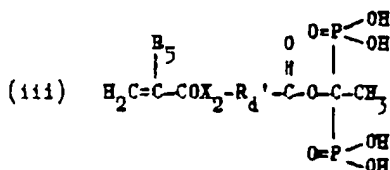
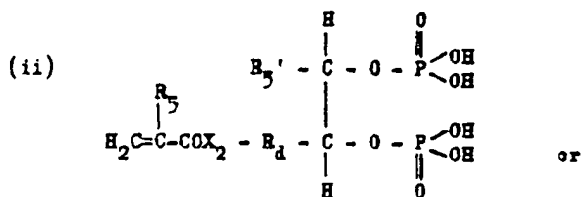
#### Example 8

A cylindrical cavity of 4 mm in diameter and 4 mm in depth was formed on the buccal surface of a human tooth using a diamond bur, then the cavity wall was acid etched with a 40% phosphoric acid aqueous solution for a minute, washed with water, and dried. Thereafter, a paste obtained by mixing Formulations VI and V for the powder — liquid type adhesive composition in Example 3 at a ratio by weight of 3:1 was filled into this cavity. Ten minutes after the curing, the sample was dipped in water at 37°C, and when the degree of the dye penetration into the bonded intersurface was examined according to the method in Example 4, the penetration was hardly observed.

#### Claims

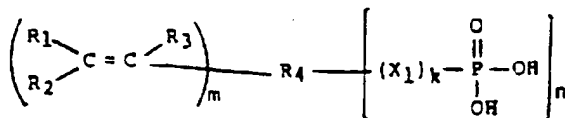
1. An adhesive composition suitable for bonding two or more adherends to one another, or for forming adhesive coatings on the surfaces of adherends, or for forming adhesive fillings in the repair of hard tissues of the living body, comprising (a) 1 part by weight of a compound of the general formula:





in which each of  $R_5$  and  $R_5'$  represents a hydrogen atom or a methyl radical,  $R_5$  represents a bivalent organic residue of 2—54 carbon atoms,  $R_d$  represents a bivalent organic residue of 4—57 carbon atoms,  $R_d'$  represents a bivalent organic residue of 3—57 carbon atoms and  $X_2$  represents O, S or  $NR_6$  where  $R_6$  represents H or  $C_{1-4}$  alkyl, and (b) 0—199 parts by weight of a vinyl monomer copolymerizable with the aforesaid compound.

2. A composition according to Claim 1 in which the compound (a) has the formula (i).
3. A composition according to Claim 1 in which the compound (a) has the formula (ii).
4. A composition according to Claim 1 in which the compound (a) has the formula (iii).
5. A composition as claimed in any one of the preceding claims that further contains 0.01—20 parts by weight of a curing agent per 100 parts by weight of the polymerizable monomers [(a) + (b)].
6. A composition as claimed in Claim 5 in which the curing agent is a redox type polymerization initiator.
7. A composition as claimed in Claim 5 in which the curing agent is a photosensitizer.
8. A composition as claimed in any one of the preceding claims that further contains a volatile organic solvent having a boiling point of 150°C or below at 760 Torr (1013 Pa) in an amount not exceeding 300 times by weight that of the polymerizable monomers [(a) + (b)].
9. A composition as claimed in any one of the preceding claims that further contains 20—500 parts by weight of a filler per 100 parts by weight of the polymerizable monomers [(a) + (b)].
10. A composition as claimed in any one of the preceding claims in which the vinyl monomer (b) is of the (meth)acrylate or styrene type or is vinyl acetate.
11. For use in applying to the wall of a tooth cavity before filling a dental composite resin in the tooth cavity, a dental adhesive composition suitable for bonding a tooth to a dental filling or for forming an adhesive coating on the surface of a tooth or for forming an adhesive filling in the repair of a tooth comprising (a) 1 part by weight of a compound of the general formula:

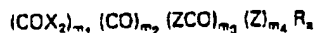


where

each of  $R_1$  and  $R_2$ , which are the same or different, represents a hydrogen atom, a  $C_{1-6}$  hydrocarbon or halogen-substituted hydrocarbon group, a group of formula  $COOR'$  where  $R'$  represents a  $C_{1-20}$  hydrocarbon or halogen-substituted hydrocarbon group or a halogen atom;

$R_3$  represents a hydrogen or halogen atom, a  $C_{1-6}$  hydrocarbon or halogen-substituted hydrocarbon group, or a CN residue, and may be the same as or different from  $R_1$  and/or  $R_2$ ;

$R_4$  represents a radical of formula:



where

$R_4$  represents a  $C_{4-40}$  organic residue having a valency of  $m + n$ , each of  $m_1$ ,  $m_2$ ,  $m_3$  and  $m_4$  represents 0, 1, 2, 3 or 4 such that  $m_1 + m_2 + m_3 + m_4 \leq m$ ,  $X_2$  represents O, S or  $NR_6$  (where  $R_6$  represents H or  $C_{1-4}$  alkyl) and Z represents O or S;

$X_1$  is a defined for  $X_2$  and may the same as or different from  $X_2$ ;

$m$  represents 1, 2, 3 or 4;

$n$  is 2, 3, 4, 5 or 8, and

**k is 0 or 1;**

5 and when  $m$  is 2 or more, each of the  $R_1$ s,  $R_2$ s and  $R_3$ s may be the same or different and when more than one  $X_1$  and/or  $X_2$  are present, each of them may be the same or different; and

(b) 0—199 parts by weight of a vinyl monomer, 0.01—20 parts by weight of a curing agent per 100 parts by weight of the polymerizable monomers [(a) + (b)], and, optionally, one or more of a redox polymerization initiator, a photosensitizer, and a volatile organic solvent having a boiling point of 150°C or below at 760 Torr (1013 Pa) in an amount not exceeding 300 times by weight that of the polymerizable monomers [(a) + (b)].

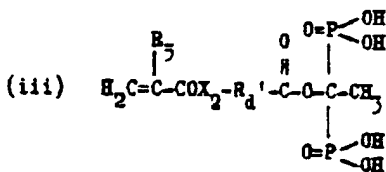
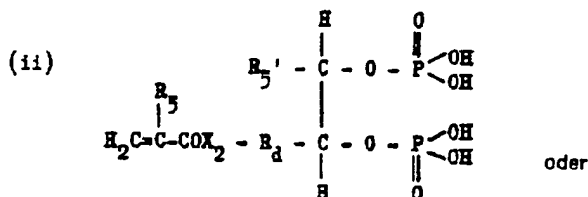
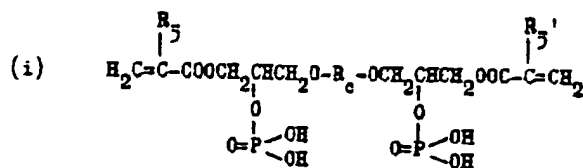
12. For use in coating the surface of a tooth for dental caries prevention, a dental adhesive composition as defined in Claim 11.

13. For use in filling into a tooth cavity, a dental adhesive composition as defined in Claim 11.

15 14. For use in bonding between a tooth and a dental restorative material or between dental restorative materials to each other, a dental adhesive composition as defined in Claim 11.

## Patentansprüche

20 1. Klebstoffmasse, die zum Verbinden von zwei oder mehreren Klebefläche miteinander oder zur Bildung von Klebeüberzügen auf den Oberflächen von Klebeflächen oder zur Bildung von klebenden Füllungen bei der Reparatur von harten Geweben des menschlichen Körpers geeignet ist aus (1) 1 Gewichtsteil einer Verbindung der allgemeinen Formel



55 worin jeweils  $R_3$  und  $R_3'$  ein Wasserstoffatom oder ein Methylrest sind,  $R_6$  einen bivalenten organischen Rest mit 2 bis 54 Kohlenstoffatomen bedeutet,  $R_4$  ein bivalenter organischer Rest mit 4 bis 57 Kohlenstoffatomen ist,  $R_2$  ein bivalenter organischer Rest mit 3 bis 57 Kohlenstoffatomen ist und  $X_2$  O, S oder  $NR_5$  bedeutet, wobei  $R_5$  H oder  $C_{1-4}$ -Alkyl ist, und (b) 0 bis 199 Gewichtsteilen eines Vinylmonomeren, das mit der vorstehend erwähnten Verbindung copolymerisierbar ist.

60 2. Masse nach Anspruch 1, dadurch gekennzeichnet, daß die Verbindung (a) der Formel (i) entspricht.

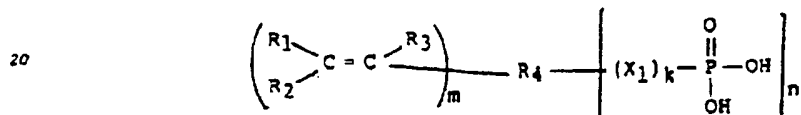
3. Masse nach Anspruch 1, dadurch gekennzeichnet, daß die Verbindung (a) der Formel (II) entspricht.

4. Masse nach Anspruch 1, dadurch gekennzeichnet, daß die Verbindung (a) der Formel (iii) entspricht.

5. Masse nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß sie außerdem

0,01 bis 20 Gewichtsteile eines Härtungsmittels pro 100 Gewichtsteile der polymerisierbaren Monomeren  
65 [(a) + (b)] enthält.

6. Masse nach Anspruch 5, dadurch gekennzeichnet, daß das Härtungsmittel ein Redoxtyp-Polymerisations-initiator ist.
7. Masse nach Anspruch 5, dadurch gekennzeichnet, daß das Härtungsmittel ein Photosensibilisator ist.
8. Masse nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß sie außerdem ein flüchtiges organisches Lösungsmittel mit einem Siedepunkt von 150°C oder darunter bei 760 Torr (1013 Pa) in einer Menge enthält, die nicht das 300-fache des Gewichts der polymerisierbaren Monomeren [(a) + (b)] übersteigt.
9. Masse nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß sie außerdem 20 bis 500 Gew.-Teile eines Füllstoffs pro 100 Gew.-Teile der polymerisierbaren Monomeren [(a) + (b)] enthält.
10. Masse nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Vinylmonomere (b) dem (Meth)acrylat oder Styrol-Typ entspricht oder aus Vinylacetate besteht.
11. Verwendung einer Dentalklebmasse, die zum Verbinden eines Zahns mit einer Zahnfüllung oder zur Bildung eines Klebstoffüberzugs auf der Oberfläche eines Zahns oder zur Bildung einer Klebstofffüllung bei der Reparatur eines Zahns geeignet ist, aus (a) 1 Gew.-Teil einer Verbindung der allgemeinen Formel



- 25 worin jeweils  $R_1$  und  $R_2$ , die gleich oder verschieden sind, für ein Wasserstoffatom, eine  $C_{1-9}$ -Kohlenwasserstoff- oder Halogen-substituierte Kohlenwasserstoffgruppe, ein Gruppe der Formel  $COOR'$  stehen, wobei  $R'$  eine  $C_{1-20}$ -Kohlenwasserstoffgruppe oder eine Halogensubstituierte Kohlenwasserstoffgruppe oder ein Halogenatom ist,  $R_3$  Wasserstoff oder ein Halogenatom, eine  $C_{1-9}$ -Kohlenwasserstoff- oder Halogen-substituierte Kohlenwasserstoffgruppe oder einen CN-Rest bedeutet und die gleiche Bedeutung wie  $R_1$  und/oder  $R_2$  oder eine andere Bedeutung wie  $R_1$  und/oder  $R_2$  besitzen kann,  $R_4$  ein Rest der Formel



ist, worin

- 30  $R_4$  einen  $C_{8-50}$ -organischen Rest mit einer Wertigkeit von  $m + n$  bedeutet, wobei jeweils  $m_1, m_2, m_3$  und  $m_4$  0, 1, 2, 3 oder 4 derart bedeuten, daß  $m_1 + m_2 + m_3 + m_4 \leq m$ ,  $X_2$  O, S oder  $NR_5$  bedeuten, (wobei  $R_5$  H oder  $C_{1-4}$ -Alkyl ist) und Z O oder S ist;

$X_1$  der Definition von  $X_2$  entspricht und die gleiche Bedeutung wie  $X_2$  oder eine andere Bedeutung wie  $X_2$  haben kann,

- 45  $m$  1, 2, 3 oder 4 ist,  
 $n$  2, 3, 4, 5 oder 6 ist und  
 $k$  0 oder 1 ist, und  
falls  $m$  2 oder mehr ist, jeder der Substituenten  $R_1, R_2$  und  $R_3$  gleich oder verschieden sein kann, und wenn mehr als einer der Substituenten  $X_1$  und/oder  $X_2$  vorliegen, jeder von ihnen gleich oder verschieden sein kann, und

- 50 (b) 0 bis 199 Gew.-Teilen eines Vinylmonomeren, 0,01 bis 20 Gew.-Teilen eines Härtungsmittels pro 100 Gew.-Teile der polymerisierbaren Monomeren [(a) + (b)] und gegebenenfalls einem oder mehreren der aus einem Redoxpolymerisationsinitiator, einem Photosensibilisator und einem flüchtigen organischen Lösungsmittel mit einem Siedepunkt von 150°C oder darunter bei 760 Torr (1013 Pa) in einer Menge, die nicht das 300-fache des Gewichts der polymerisierbaren Monomeren [(a) + (b)] übersteigt, bestehenden Bestandteile, zur Aufbringung auf die Wand einer Zahnkavität vor dem Einfüllen eines Dentalkompositharzes in die Zahnkavität.

12. Verwendung einer Dentalklebmasse gemäß Anspruch 1 zum Beschichten der Oberfläche eines Zahns für eine Verhinderung einer Zahnkaries.

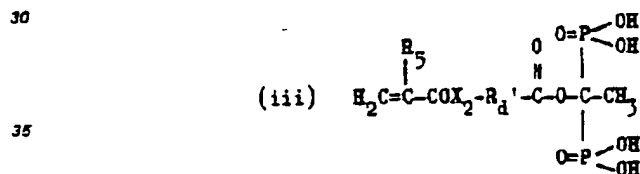
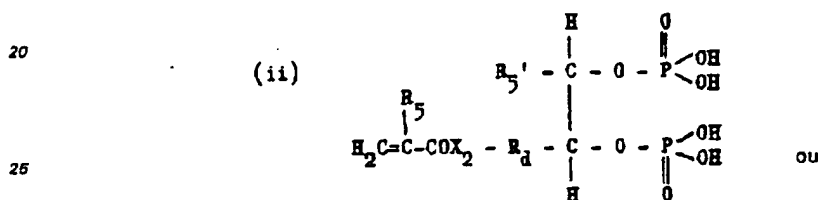
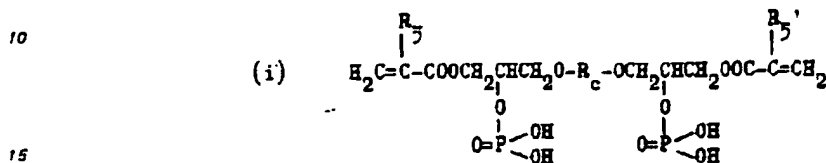
13. Verwendung einer Dentalklebmasse gemäß Anspruch 9 zum Einfüllen in eine Zahnkavität.

- 60 14. Verwendung einer Dentalklebmasse gemäß Anspruch 9 zum Verbinden eines Zahns mit einem Zahnreparaturmaterial oder zum Verbinden von Zahnreparaturmaterialien miteinander.

## Revendications

1. Une composition adhésive appropriée à l'union de deux ou plus de deux surfaces à coller entre elles, ou à la formation de revêtements adhésifs sur des surfaces à coller, ou à la formation d'obturations adhésives dans la réparation de tissus durs de l'organisme vivant, comprenant

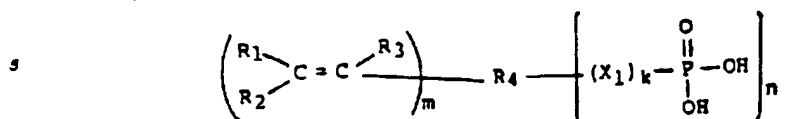
(a) 1 partie en poids d'un composé de formule générale:



où chacun de  $R_5$  et  $R_5'$  représente un atome d'hydrogène ou un radical méthyle,  $R_c$  représente un reste organique bivalent de 2 à 54 atomes de carbone,  $R_d$  représente un reste organique bivalent de 4 à 57 atomes de carbone,  $R_d'$  représente un reste organique bivalent de 3 à 57 atomes de carbone et  $X_2$  représente O, S ou  $NR_6$  où  $R_6$  représente H ou un alcoyle en  $C_{1-4}$  et (b) 0 à 199 parties en poids d'un monomère vinylique copolymérisable avec le composé précité.

2. Une composition selon la revendication 1 dans laquelle le composé (A) répond à la formule (ii).
3. Une composition selon la revendication 1 dans laquelle le composé (A) répond à la formule (iii).
4. Une composition selon la revendication 1 dans laquelle le composé (A) répond à la formule (iii).
5. Une composition comme revendiqué dans l'une quelconque des revendications précédentes qui contient de plus 0,01 à 20 parties en poids d'un agent de durcissement pour 100 parties en poids des monomères polymérisables [(a) + (b)].
6. Une composition comme revendiqué dans la revendication 5 dans laquelle l'agent de durcissement est un amorceur de polymérisation de type redox.
7. Une composition comme revendiqué dans la revendication 5 dans laquelle l'agent de durcissement est un photosensibilisateur.
8. Une composition comme revendiqué dans l'une quelconque des revendications précédentes qui contient de plus un solvant organique volatil ayant un point d'ébullition de 150°C ou moins à 760 torrs (1013 Pa) en une quantité ne dépassant pas 300 fois en poids celle des monomères polymérisables [(a) + (b)].
9. Une composition comme revendiqué dans l'une quelconque des revendications précédentes qui contient de plus 20 à 500 parties en poids d'une charge pour 100 parties en poids des monomères polymérisables [(a) + (b)].
10. Une composition comme revendiqué dans l'une quelconque des revendications précédentes dans laquelle le monomère vinylique (b) est de type (méth)acrylate ou styrène ou est l'acétate de vinyle.
11. Pour l'emploi dans l'application à la paroi d'une cavité dentaire avant l'obturation de la cavité dentaire avec une résine composite dentaire, une composition adhésive dentaire appropriée à l'union d'une dent à une obturation dentaire ou à la formation d'un revêtement adhésif sur la surface d'une dent ou

à la formation d'une obturation adhésive dans la réparation d'une dent comprenant (a) 1 partie en poids d'un composé de formule générale:

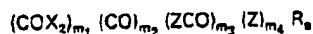


dans laquelle

chacun de  $R_1$  et  $R_2$ , qui sont semblables ou différents, représente un atome d'hydrogène, un groupe hydrocarboné en  $C_{1-5}$  ou un groupe hydrocarboné halogénosubstitué, un groupe de formule  $COOR'$  dans laquelle  $R'$  représente un groupe hydrocarboné en  $C_{1-50}$  ou un groupe hydrocarboné halogéno-substitué ou un atome d'halogène;

$R_3$  représente un hydrogène ou un atome d'halogène, un groupe hydrocarboné en  $C_{1-5}$  ou un groupe hydrocarboné halogéno-substitué, ou un reste CN, et peut être semblable ou différent de  $R_1$  et/ou  $R_2$ ;

$R_4$  représente un radical de formule:



où

$R_5$  représente un reste organique en  $C_{8-50}$  ayant une valence de  $m + n$ , chacun de  $m_1$ ,  $m_2$ ,  $m_3$  et  $m_4$  représente 0, 1, 2, 3 ou 4 pour que  $m_1 + m_2 + m_3 + m_4 \leq m$ ,  $X_2$  représente O, S ou  $NR_6$  (où  $R_6$  représente H ou un alcoyle en  $C_{1-4}$ ) et Z représente O ou S;

$X_1$  est comme défini pour  $X_2$  et peut être semblable ou différent de  $X_2$ ;

$m$  représente 1, 2, 3 ou 4;

$n$  est 2, 3, 4, 5 ou 6, et

$k$  est 0 ou 1;

et, lorsque  $m$  est 2 ou plus, les  $R_1$ ,  $R_2$  et  $R_3$ ,  $R_4$  peuvent chacun être semblables ou différents, et, lorsque plus d'un  $X_1$  et/ou  $X_2$  est présente, ils peuvent chacun être semblables ou différents; et

(b) 0 à 199 parties en poids d'un monomère vinylique, 0,01 à 20 parties en poids d'un agent de durcissement pour 100 parties en poids des monomères polymérisables [(a) + (b)], et éventuellement un ou plusieurs d'un amorceur de polymérisation redox, un photosensibilisateur et un solvant organique volatil ayant un point d'ébullition de 150°C ou moins à 760 torrs (1 013 Pa) en une quantité ne dépassant pas 300 fois le poids des monomères polymérisables [(a) + (b)].

12. Pour l'emploi dans le revêtement de la surface d'une dent pour la prévention des caries dentaires, une composition adhésive dentaire comme défini dans la revendication 11.

13. Pour l'emploi dans l'obturation d'une cavité dentaire, une composition adhésive dentaire comme défini dans la revendication 11.

14. Pour l'emploi dans l'union d'une dent et d'une matière restauratrice dentaire ou de matières restauratrices dentaires entre elles, une composition adhésive dentaire comme défini dans la revendication 11.